II. REVIEW OF BASIC QUANTUM MECHANICS: DYNAMIC BEHAVIOR OF QUANTUM SYSTEMS:

QUANTUM MECHANICAL EQUATIONS OF MOTION:

To this point our review, we have been concerned with describing the states of a system at one instant of time. The complete dynamical theory must describe, of course, connections between different instants of time.

> "When one makes an observation on the dynamical system, the state of the system gets changed in an unpredictable way, but in between observations causality applies, in quantum mechanics as in classical mechanics, and the system is governed by equations of motion which make the state at one time determined the state at a later time." [10]

Thus, it is only the disturbance caused by the interaction of a system with a measuring device that makes the system's behavior cease to be strictly causal.

SCHRÖDINGER EQUATION OF MOTION:

Consider the time evolution of a particular state of an undisturbed system. To deal with such a dynamical system, we need a linear operator of the form[11]

$$\left|\psi(t)\right\rangle = \mathcal{T}\ (t,t_0)\ \left|\psi(t_0)\right\rangle \qquad [\text{ II-1 }]$$

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[10] From Section 27 of P. A. M. Dirac, *The Principles of Quantum Mechanics* (Revised fourth edition), Oxford University Press (1967).

[11] This is first member of a class of "displacement " operators that we may treat in a similar fashion. See Section 25 of P. A. M. Dirac, *The Principles of Quantum Mechanics* (Revised fourth edition), Oxford University Press (1967).

Passing to the limit $t \to t_0$, this operator yields a related linear operator for the time derivative of the state vector with respect to t_0

$$\frac{d}{dt_0}\left|\psi(t_0)\right\rangle = \left\{\lim_{t\to t_0}\frac{\mathcal{T}(t,t_0)-1}{t-t_0}\right\}\left|\psi(t_0)\right\rangle = \mathcal{O}p(t_0)\left|\psi(t_0)\right\rangle \qquad \text{[II-2a]}$$

<u>If it is postulated that</u> $\mathcal{O}p(t) = (i\hbar)^{-1}\mathcal{H}(t)$ where $\mathcal{H}(t)$ is the total Hamiltonian (energy) of the system,[12] we obtain the Schrödinger equation of motion in abstract form -- *viz.*

$$i\hbar\frac{d}{dt}\left|\psi(t)\right\rangle = \mathcal{H}(t)\left|\psi(t)\right\rangle \qquad \text{[II-2b]}$$

Equations [II-1] and [II-2b] are consistent if

$$i\hbar\frac{d}{dt}\mathcal{T}(t,t_0) = \mathcal{H}(t)\,\mathcal{T}(t,t_0)\ . \qquad \text{[II-3]}$$

In the **Schrödinger representation**, the abstract **Schrödinger equation of motion** becomes[13]

$$i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t) = \left\langle\vec{r}\right|\mathcal{H}(t)\left|\vec{r}\right\rangle\psi(\vec{r},t) \qquad \text{[II-4]}$$

<u>HEISENBERG EQUATION OF MOTION:</u>

In the ***Schrödinger picture***, as outlined above, we picture the states of the undisturbed motion by associating each state with a moving ket, the state at any time

[12] There are two justifications of this postulate: (a) analogy with classical mechanics (see Equation [II-6]) and (b) relativistic invariance *vis-a-vis* Equation [I-20].

[13] Since $$\left|\psi(t)\right\rangle = \iiint d\vec{r}\left|\vec{r}\right\rangle\left\langle\vec{r}\right|\psi(t)\rangle = \iiint d\vec{r}\left|\vec{r}\right\rangle\psi(\vec{r},t)$$

corresponding to the ket at that time. In the ***Heisenberg picture*** a unitary transformation is applied which brings to rest the kets corresponding to states of undisturbed motion. In this picture, the appropriate equation of motion is one describing the motion or evolution of linear operators (dynamic variables) -- *viz*.

$$\mathcal{O}p_t = \mathcal{T}^{-1}\mathcal{O}p\,\mathcal{T} \quad \text{or} \quad \mathcal{T}\,\mathcal{O}p_t = \mathcal{O}p\,\mathcal{T} \qquad \text{[II-5a]}$$

where $\mathcal{O}p$ is a fixed *Schrödinger dynamic variable* and $\mathcal{O}p_t$ is a time varying *Heisenberg dynamic variable*. Differentiating with respect to time

$$\frac{d\mathcal{T}}{dt}\mathcal{O}p_t + \mathcal{T}\frac{d\mathcal{O}p_t}{dt} = \mathcal{O}p\,\frac{d\mathcal{T}}{dt} \qquad \text{[II-5b]}$$

and then using Equation [II-3], we obtain the Heisenberg form of the equation of motion as

$$i\hbar\frac{d\mathcal{O}p_t}{dt} = \mathcal{T}^{-1}\mathcal{O}p\,\mathcal{H}\,\mathcal{T} - \mathcal{T}^{-1}\mathcal{H}\,\mathcal{T}\,\mathcal{O}p_t = \left[\mathcal{O}p_t, \mathcal{H}_t\right] \qquad \text{[II-6]}$$

where $\mathcal{H}_t = \mathcal{T}^{-1}\mathcal{H}\,\mathcal{T}$. Note that this equation -- *i.e.* Equation [II-6] -- is consistent with the classical analogy discussed earlier.

<u>ENERGY EIGENVECTOR REPRESENTATION -- THE HEISENBERG REPRESENTATION</u>:
In the Heisenberg picture the stationary states $|E_n\rangle$ correspond to fixed eigenvectors of a time independent Hamiltonian .

<u>CASE 1</u> -- Time independent Hamiltonian:

To study the time evolution of a given state when the Hamiltonian is time independent, we expand the state vector in terms of these fixed energy eigenvectors and write Equation [II-2b] as

$$i\hbar\frac{d}{dt}\left|\psi(t)\right\rangle = \mathcal{H}\left|\psi(t)\right\rangle = \sum_n \mathcal{H}\left|E_n\right\rangle\left\langle E_n\middle|\psi(t)\right\rangle = \sum_n E_n\left|E_n\right\rangle\left\langle E_n\middle|\psi(t)\right\rangle \qquad \text{[II-7a]}$$

and

$$i\hbar\frac{\partial}{\partial t}\left\langle E_n\middle|\psi(t)\right\rangle = \sum_{n'} E_{n'}\left\langle E_n\middle|E_{n'}\right\rangle\left\langle E_{n'}\middle|\psi(t)\right\rangle = E_n\left\langle E_n\middle|\psi(t)\right\rangle . \qquad \text{[II-7b]}$$

Therefore

$$\begin{aligned}\left\langle E_n\middle|\psi(t)\right\rangle &= \left\langle E_n\middle|\psi(0)\right\rangle \exp\left(\frac{E_n t}{i\hbar}\right) = \left\langle E_n\middle|\psi(0)\right\rangle \exp(-i\omega_n t) \\ &= C_n(0)\exp(-i\omega_n t)\end{aligned} \qquad \text{[II-8]}$$

We may expand an arbitrary wave function in terms of these eigenvectors -- *viz*.

$$\begin{aligned}\psi(\vec{r},t) &= \left\langle \vec{r}\middle|\psi(t)\right\rangle = \sum_n \left\langle \vec{r}\middle|E_n\right\rangle\left\langle E_n\middle|\psi(t)\right\rangle = \sum_n \left\langle E_n\middle|\psi(0)\right\rangle\left\langle \vec{r}\middle|E_n\right\rangle \exp(-i\omega_n t) \\ &= \sum_n C_n(0)\; u_n(\vec{r})\,\exp(-i\omega_n t)\end{aligned} \qquad \text{[II-9]}$$

where $u_n(\vec{r}) \equiv \left\langle \vec{r}\middle|E_n\right\rangle$ and the coefficients $C_n(0) = \left\langle E_n\middle|\psi(0)\right\rangle$ are, **in this instance,** of course independent of time.

CASE 2 -- Time dependent Hamiltonian:

Consider now a time dependent Hamiltonian in the form

$$\mathcal{H}(t) = \mathcal{H}_0 + \mathcal{H}_1(t) \qquad \text{[II-10]}$$

In this instance, we may write Equation [II-2b] as

$$\begin{aligned}i\hbar\frac{d}{dt}\left|\psi(t)\right\rangle &= \sum_n \mathcal{H}_0\left|E_n\right\rangle\left\langle E_n\middle|\psi(t)\right\rangle + \sum_n \mathcal{H}_1(t)\left|E_n\right\rangle\left\langle E_n\middle|\psi(t)\right\rangle \\ &= \sum_n E_n\left|E_n\right\rangle\left\langle E_n\middle|\psi(t)\right\rangle + \sum_n \mathcal{H}_1(t)\left|E_n\right\rangle\left\langle E_n\middle|\psi(t)\right\rangle\end{aligned} \qquad \text{[II-11a]}$$

which becomes, on operating from the left with $\langle E_{n'}|$

$$i\hbar \frac{d}{dt} \langle E_{n'}|\psi(t)\rangle = \sum_n E_n \langle E_{n'}|E_n\rangle\langle E_n|\psi(t)\rangle + \sum_n \langle E_{n'}|\mathcal{H}_1(t)|E_n\rangle\langle E_n|\psi(t)\rangle \quad \text{[II-11b]}$$

If we write $\langle E_n|\psi(t)\rangle = C_n(t)\, \exp(-i\omega_n t)$ -- see Equation [II-8] -- then

$$\left[i\hbar\, \dot{C}_n(t) + E_n\, C_n(t)\right] \exp(-i\omega_n t) = E_n\, C_n(t) \exp(-i\omega_n t) + \sum_{n'} \langle E_n|\mathcal{H}_1(t)|E_{n'}\rangle C_{n'}(t) \exp(-i\omega_{n'} t) \quad \text{[II-11c]}$$

Therefore, when we expand an arbitrary wave function *a la* Equation [II-9], we find

$$\langle \vec{r}|\psi(t)\rangle = \sum_n \langle \vec{r}|E_n\rangle\langle E_n|\psi(t)\rangle = \sum_n C_n(t) \langle \vec{r}|E_n\rangle \exp(-i\omega_n t) = \sum_n C_n(t)\, u_n(\vec{r})\, \exp(-i\omega_n t) \quad \text{[II-12a]}$$

and

$$\dot{C}_n(t) = -\frac{i}{\hbar} \sum_{n'} C_{n'}(t) \langle E_n|\mathcal{H}_1(t)|E_{n'}\rangle \exp(i\,\omega_{nn'} t) \quad \text{[II-12b]}$$

where $\omega_{nn'} = \omega_n - \omega_{n'}$ and

$$\langle E_n|\mathcal{H}_1(t)|E_{n'}\rangle = \iiint d\vec{r}\, u_n(\vec{r})\, \mathcal{H}_1(t)\, u_{n'}(\vec{r}) \,. \quad \text{[II-13]}$$

If we write $c_n(t) = C_n(t)\, \exp(-i\,\omega_n t)$, $c_n(t)$ obeys the equation of motion

$$\dot{c}_n(t) = -i\,\omega_n\, c_n(t) - \frac{i}{\hbar} \sum_{n'} c_{n'}(t) \langle E_n|\mathcal{H}_1(t)|E_{n'}\rangle \quad \text{[II-14]}$$

TIME DEPENDENT PERTURBATION THEORY:

ELEMENTARY IDEAS -- FIRST ORDER ITERATION:

In set of equations denoted as Equation [II-12b] assume that

$$C_i(0) = 1 \quad \text{and} \quad C_n(0) = 0 \ \text{ for } \ n \neq i \qquad \text{[II-15]}$$

so that in first-order

$$\dot{C}_n(t) \approx \dot{C}_n^{(1)}(t) = -\frac{i}{\hbar} \langle E_n | \mathcal{H}_1(t) | E_i \rangle \exp\left(i\,\omega_{ni}\, t \right) \qquad \text{[II-16]}$$

Suppose that

$$\mathcal{H}_1(t) = \mathcal{V}_0 \cos\omega_r t = \mathcal{V}_0 \left\{ \frac{\exp(i\omega_r t) + \exp(-i\omega_r t)}{2} \right\} \qquad \text{[II-17]}$$

for $t \geq 0$, then

$$C_n(t) \approx C_n^{(1)}(t) = -i \frac{\langle E_n | \mathcal{V}_0 | E_i \rangle}{2\hbar} \left\{ \frac{\exp\left[i\left(\omega_{ni} + \omega_r\right) t \right] - 1}{i\left(\omega_{ni} + \omega_r\right)} + \frac{\exp\left[i\left(\omega_{ni} - \omega_r\right) t \right] - 1}{i\left(\omega_{ni} - \omega_r\right)} \right\} \qquad \text{[II-18]}$$

CASE 1: $\omega_r = 0$

$$\left| C_n^{(1)}(t) \right|^2 = \frac{\left| \langle E_n | \mathcal{V}_0 | E_i \rangle \right|^2}{\hbar^2} \frac{\sin^2\left(\omega_{ni}\, t/2\right)}{\left(\omega_{ni}/2\right)^2} \qquad \text{[II-19]}$$

which is valid as long as $C_i(t) \approx 1$. Equation [II-18] **shows that transitions are more likely if energy is conserved between initial and final states**.

CASE 2: $\omega_r \neq 0$

In the so called ***rotating-wave approximation*** we neglect the first term in Equation [II-18] so that

$$\left|C_n^{(1)}(t)\right|^2 = \frac{\left|\langle E_n|\mathcal{V}_0|E_i\rangle\right|^2}{4\hbar^2}\,\frac{\sin^2\left[\left(\omega_{ni}-\omega_r\right)t/2\right]}{\left[\left(\omega_{ni}-\omega_r\right)/2\right]^2} \qquad \text{[II-20]}$$

which is again valid as long as $C_i(t) \approx 1$. This equation **shows that transitions are unlikely unless the resonance condition $\omega_r \approx \omega_{ni}$ is satisfied.**

Let us suppose that we have continuum of energy levels represented by a density of states function $\rho\,(\omega)$. Therefore the total probability for transition out of the initial state has the approximate value

$$\mathrm{P}_T = \int \rho\,(\omega)\left|C_n^{(1)}(t)\right|^2 d\omega = \int \rho\,(\omega)\,\frac{\left|\mathcal{V}\,(\omega)\right|^2}{4\hbar^2}\,t^2\,\frac{\sin^2\left[\left(\omega-\omega_r\right)t/2\right]}{\left[\left(\omega-\omega_r\right)t/2\right]^2}\,d\omega \qquad \text{[II-21a]}$$

For $\left(\omega-\omega_r\right)t << \pi$

$$\mathrm{P}_T \approx t^2 \int \rho(\omega)\,\frac{\left|\mathcal{V}\,(\omega)\right|^2}{4\hbar^2}\,d\omega \qquad \text{[II-21b]}$$

so that initial the transition rate -- *i.e.,* $\dfrac{d\,\mathrm{P}_T}{dt}$ -- is linearly dependent on t. For longer times, it is reasonable to assume that the "frequency-width" of $\rho(\omega)\left|\mathcal{V}\,(\omega)\right|^2$ is large compared to the inverse of the elapsed time -- or more precisely $\dfrac{\pi}{t}$ --we may further approximate the total transition probability as

$$\mathrm{P}_T \approx \rho(\omega_r)\,\frac{\left|\mathcal{V}\,(\omega_r)\right|^2}{2\hbar^2}\,t\int_{-\infty}^{+\infty}\frac{\sin^2 u}{u^2}\,du \approx \frac{\pi}{2\hbar^2}\,\rho(\omega_r)\left|\mathcal{V}\,(\omega_r)\right|^2 t \qquad \text{[II-21c]}$$

which yields the famous **Fermi Golden Rule** for the transition rate

$$\Gamma = \frac{d\,\mathrm{P}_T}{dt} = -\frac{d}{dt}\left|C_i^{(1)}\right|^2 = \frac{\pi}{2\hbar^2}\,\rho(\omega_r)\left|\mathcal{V}(\omega_r)\right|^2 \qquad \text{[II-22]}$$

HIGHER-ORDER TIME DEPENDENT PERTURBATION THEORY:

Consider once again perturbation solutions for a Hamiltonian of the form $\mathcal{H}(t) = \mathcal{H}_0 + \mathcal{H}_1(t)$. At outset we transform our equations to the *halfway land* of the **interaction picture** by first rewriting Equation [II-2b] to emphasize that it deals with a state vector in the Schrödinger picture -- *viz*.

$$i\hbar\frac{d}{dt}\left|\psi_S(t)\right\rangle = \mathcal{H}\left|\psi_S(t)\right\rangle \qquad \text{[II-2b']}$$

Then we make the unitary transformation

$$\left|\psi_S(t)\right\rangle = \mathcal{T}_0(t)\left|\psi_I(t)\right\rangle = \exp\left(-i\mathcal{H}_0\, t/\hbar\right)\left|\psi_I(t)\right\rangle \qquad \text{[II-23]}$$

so that Equation [II-2b'] becomes

$$i\hbar\frac{d\mathcal{T}_0(t)}{dt}\left|\psi_I(t)\right\rangle + i\hbar\,\mathcal{T}_0(t)\frac{d}{dt}\left|\psi_I(t)\right\rangle = \mathcal{T}_0(t)\,\mathcal{H}_0\left|\psi_I(t)\right\rangle + \mathcal{H}_1(t)\,\mathcal{T}_0(t)\left|\psi_I(t)\right\rangle \qquad \text{[II-24]}$$

Using a version of Equation [II-3] we obtain the equation of motion for the state in the interaction picture -- *viz*.

$$\frac{d}{dt}\left|\psi_I(t)\right\rangle = -\frac{i}{\hbar}\mathcal{T}_0^{\dagger}(t)\,\mathcal{H}_1(t)\,\mathcal{T}_0(t)\left|\psi_I(t)\right\rangle = -\frac{i}{\hbar}\mathcal{H}_1^{\,I}(t)\left|\psi_I(t)\right\rangle \qquad \text{[II-25]}$$

If we write

$$\left|\psi_I(t)\right\rangle = \mathcal{T}_I(t)\left|\psi_I(0)\right\rangle \qquad \text{[II-26a]}$$

so that

$$\frac{d}{dt}\,\mathcal{T}_I(t) = -\frac{i}{\hbar}\,\mathcal{H}_1^{\,I}(t)\,\mathcal{T}_I(t) \qquad \text{[II-26b]}$$

We may formally integrate this equation to obtain

$$\mathcal{T}_I(t) = 1 + \left(-\frac{i}{\hbar}\right)\int_0^t dt'\,\mathcal{H}_1^{\,I}(t')\,\mathcal{T}_I(t') \qquad \text{[II-27a]}$$

By iterating once we have

$$\mathcal{T}_I(t) = 1 + \left(\frac{i}{\hbar}\right)\int_0^t dt_1\,\mathcal{H}_1^{\,I}(t_1) + \left(\frac{i}{\hbar}\right)^2\int_0^t dt_1\,\mathcal{H}_1^{\,I}(t_1)\int_0^{t_1} dt_2\,\mathcal{H}_1^{\,I}(t_2)\,\mathcal{T}_I(t_2) \qquad \text{[II-27b]}$$

or by successive iterations we have to an arbitrary level of precision

$$\begin{aligned}\mathcal{T}_I(t) = 1 &+ \left(\frac{i}{\hbar}\right)\int_0^t dt_1\,\mathcal{H}_1^{\,I}(t_1) + \left(\frac{i}{\hbar}\right)^2\int_0^t dt_1\,\mathcal{H}_1^{\,I}(t_1)\int_0^{t_1} dt_2\,\mathcal{H}_1^{\,I}(t_2)\\ &+ \left(\frac{i}{\hbar}\right)^3\int_0^t dt_1\,\mathcal{H}_1^{\,I}(t_1)\int_0^{t_1} dt_2\,\mathcal{H}_1^{\,I}(t_2)\int_0^{t_2} dt_3\,\mathcal{H}_1^{\,I}(t_3) + \cdots\cdots\end{aligned} \qquad \text{[II-27c]}$$

DENSITY OPERATOR (MATRIX):

In classical theory any state of a dynamic system is represented as a point in the *phase space* whose number of dimensions is twice (coordinate and momentum) the number of degrees of freedom in the system. This point will move according to the classical equations of motion. If the state of the system is defined by some probabilistic specification, then we know only the probability that the system may be assigned a given phase point at a particular time. We may envisage the time varying probabilistic specification as a ***fluid*** of density $\rho(q_1, q_2, q_3, \cdots p_1, p_2, p_3, \cdots, t)$ moving through phase

space. Each particle of the fluid will move according to the system's equations of motion. The following conservation relationship holds:

$$\frac{\partial \rho}{\partial t} = -\sum_r \left\{ \frac{\partial}{\partial q_r}\left[\rho \frac{dq_r}{dt}\right] + \frac{\partial}{\partial p_r}\left[\rho \frac{dp_r}{dt}\right] \right\} = -\{\rho, \mathcal{H}\}_{\mathrm{PB}} \qquad \text{[II-28]}$$

John von Neumann first introduced a corresponding density function into quantum mechanics. Dirac pointed out that the existence of such a quantum mechanical density is surprising in view of the fact that phase space has no meaning in quantum mechanics since numerical values cannot be assigned simultaneously to the coordinates and momenta. The quantum mechanical density operator (dyadic) is defined as

$$\rho = \sum_m |m\rangle P_m \langle m| \qquad \text{[II-29]}$$

where P_m is the probability of the system being in the state $|m\rangle$.

The equation of motion for the density operator is easily determined from the Schrödinger equation -- *i.e.* Equation [II-2b] -- as

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= \sum_m P_m \left\{ \frac{\partial |\dot{m}\rangle}{\partial t}\langle m| + |m\rangle \frac{\partial \langle \dot{m}|}{\partial t} \right\} \\ &= -\frac{i}{\hbar}\sum_m P_m \left\{ \mathcal{H}\, |m\rangle\langle m| - |m\rangle\langle m| \mathcal{H} \right\} \; . \\ &= -\frac{i}{\hbar}[\mathcal{H}, \rho] \end{aligned} \qquad \text{[II-30]}$$

This equation is, thus, the classical analogy of Equation [II-28]. Let us now express the expectation value of an operator $\mathcal{O}p$ in terms of the density operator -- *viz*.

$$\begin{aligned}\langle \mathcal{O}p \rangle &= \sum_{\psi} P_{\psi} \langle \psi | \mathcal{O}p \, | \psi \rangle = \sum_{\psi} P_{\psi} \sum_{m} \langle \psi | \mathcal{O}p \, | m \rangle \langle m | \psi \rangle \\ &= \sum_{m} \sum_{\psi} P_{\psi} \langle m | \psi \rangle \langle \psi | \mathcal{O}p \, | m \rangle = \sum_{m} \langle m | \rho \, \mathcal{O}p \, | m \rangle \qquad \text{[II-31]} \\ &= \mathrm{tr}\left(\rho \, \mathcal{O}p \right)\end{aligned}$$

Gibbs showed that when a dynamic system is in thermodynamic equilibrium with its surroundings at a given temperature T, the density is give by

$$\rho = \left(\text{constant}\right) \, \exp\left[-\mathcal{H} / kT \right] \; . \qquad \text{[II-32a]}$$

This formula is taken over unchanged into quantum mechanics.

$$\rho = \left(\text{constant}\right) \, \exp\left[-\mathcal{H} / kT \right] \qquad \text{[II-32b]}$$

APPENDIX - TIME INDEPENDENT PERTURBATION THEORY

Suppose that we have a Hamiltonian $\mathcal{H} = \mathcal{B} + \mathcal{S}$ where $\mathcal{B}$ is a big part and $\mathcal{S}$ is a small part. Of course, we want the solution to the complete eigenvalue problem - *i.e.*

$$\mathcal{H}\left|\mathcal{H}^n\right\rangle = \mathcal{H}^n\left|\mathcal{H}^n\right\rangle \qquad \text{[A-1]}$$

To obtain an approximate solution we expand the eigenvalues and eigenvectors in a series of terms of ***increasing smallness*** - *viz.*

$$\mathcal{H}^n = \mathcal{H}_0^n + \mathcal{H}_1^n + \mathcal{H}_2^n + \mathcal{H}_3^n + \cdots \qquad \text{[A-2a]}$$

$$\left|\mathcal{H}^n\right\rangle = \left|\mathcal{H}_0^n\right\rangle + \left|\mathcal{H}_1^n\right\rangle + \left|\mathcal{H}_2^n\right\rangle + \cdots \qquad \text{[A-2b]}$$

$$\left\langle\mathcal{H}^n\right| = \left\langle\mathcal{H}_0^n\right| + \left\langle\mathcal{H}_1^n\right| + \left\langle\mathcal{H}_2^n\right| + \cdots \qquad \text{[A-2c]}$$

Let us first consider normalization - *i.e.*

$$\left\langle\mathcal{H}^n\middle|\mathcal{H}^n\right\rangle = \left(\left\langle\mathcal{H}_0^n\right| + \left\langle\mathcal{H}_1^n\right| + \left\langle\mathcal{H}_2^n\right| + \cdots\right)\left(\left|\mathcal{H}_0^n\right\rangle + \left|\mathcal{H}_1^n\right\rangle + \left|\mathcal{H}_2^n\right\rangle + \cdots\right) = 1 \qquad \text{[A-3a]}$$

Compare terms of ***equal smallness*** so that

$$\left\langle\mathcal{H}^n\middle|\mathcal{H}^n\right\rangle = \left\langle\mathcal{H}_0^n\middle|\mathcal{H}_0^n\right\rangle = 1 \qquad \text{[A-3b]}$$

$$\left\langle\mathcal{H}_0^n\middle|\mathcal{H}_1^n\right\rangle + \left\langle\mathcal{H}_1^n\middle|\mathcal{H}_0^n\right\rangle = 0 \qquad \text{[A-3c]}$$

$$\left\langle\mathcal{H}_0^n\middle|\mathcal{H}_2^n\right\rangle + \left\langle\mathcal{H}_1^n\middle|\mathcal{H}_1^n\right\rangle + \left\langle\mathcal{H}_2^n\middle|\mathcal{H}_0^n\right\rangle = 0 \quad \textit{etc.} \qquad \text{[A-3d]}$$

From Equation [A-3c] we see that we may take $\left\langle\mathcal{H}_1^n\middle|\mathcal{H}_0^n\right\rangle = 0$ without introducing error. Next we write an expanded version of the eigenvalue equation [A-1]

$$\begin{aligned}(\mathcal{B}+\mathcal{S})&\left(\left|\mathcal{H}_0^n\right\rangle+\left|\mathcal{H}_1^n\right\rangle+\left|\mathcal{H}_2^n\right\rangle+\cdots\right)\\&=\left(\mathcal{H}_0^n+\mathcal{H}_1^n+\mathcal{H}_2^n+\mathcal{H}_3^n+\cdots\right)\left(\left|\mathcal{H}_0^n\right\rangle+\left|\mathcal{H}_1^n\right\rangle+\left|\mathcal{H}_2^n\right\rangle+\cdots\right)\end{aligned} \qquad \text{[A-4a]}$$

Again compare terms of ***equal smallness*** so that

$$\mathcal{B}\left|\mathcal{H}_0^n\right\rangle=\mathcal{H}_0^n\left|\mathcal{H}_0^n\right\rangle \qquad \text{[A-4b]}$$

$$\mathcal{S}\left|\mathcal{H}_0^n\right\rangle+\mathcal{B}\left|\mathcal{H}_1^n\right\rangle=\mathcal{H}_0^n\left|\mathcal{H}_1^n\right\rangle+\mathcal{H}_1^n\left|\mathcal{H}_0^n\right\rangle \qquad \text{[A-4c]}$$

$$\mathcal{B}\left|\mathcal{H}_2^n\right\rangle+\mathcal{S}\left|\mathcal{H}_1^n\right\rangle=\mathcal{H}_0^n\left|\mathcal{H}_2^n\right\rangle+\mathcal{H}_1^n\left|\mathcal{H}_1^n\right\rangle+\mathcal{H}_2^n\left|\mathcal{H}_0^n\right\rangle \quad etc. \qquad \text{[A-4d]}$$

Operate through Equation [A-4c] with $\left\langle\mathcal{H}_0^n\right|$ and using Equations [A-3b] and [A-4b] we find

$$\mathcal{H}_1^n=\left\langle\mathcal{H}_0^n\right|\mathcal{S}\left|\mathcal{H}_0^n\right\rangle \qquad \text{[A-5]}$$

Operate through Equation [A-4c] with $\left\langle\mathcal{H}_0^m\right|$ and using again Equations [A-3b] and [A-4b] we find

$$\left\langle\mathcal{H}_0^m\right|\mathcal{S}\left|\mathcal{H}_0^n\right\rangle=\left(\mathcal{H}_0^m-\mathcal{H}_0^n\right)\left\langle\mathcal{H}_0^m\middle|\mathcal{H}_1^n\right\rangle \qquad \text{[A-6a]}$$

or we have the **representative**

$$\left\langle\mathcal{H}_0^m\middle|\mathcal{H}_1^n\right\rangle=\frac{\left\langle\mathcal{H}_0^m\right|\mathcal{S}\left|\mathcal{H}_0^n\right\rangle}{\left(\mathcal{H}_0^m-\mathcal{H}_0^n\right)} \qquad \text{[A-6b]}$$

and

$$\left|\mathcal{H}_1^n\right\rangle=\sum_m\left|\mathcal{H}_0^m\right\rangle\left\langle\mathcal{H}_0^m\middle|\mathcal{H}_1^n\right\rangle=\sum_{m\neq n}\left|\mathcal{H}_0^m\right\rangle\frac{\left\langle\mathcal{H}_0^m\right|\mathcal{S}\left|\mathcal{H}_0^n\right\rangle}{\left(\mathcal{H}_0^m-\mathcal{H}_0^n\right)} \qquad \text{[A-6c]}$$

Operate through Equation [A-4d] with $\left\langle\mathcal{H}_0^n\right|$ and, of course, using Equations [A-3b] and [A-4b] we find

$$\left\langle \mathcal{H}_0^n \middle| \mathcal{S} \middle| \mathcal{H}_1^n \right\rangle = \mathcal{H}_1^n \left\langle \mathcal{H}_0^n \middle| \mathcal{H}_1^n \right\rangle + \mathcal{H}_2^n = \mathcal{H}_2^n \qquad [\text{ A-7a }]$$

or

$$\begin{aligned} \mathcal{H}_2^n &= \left\langle \mathcal{H}_0^n \middle| \mathcal{S} \middle| \mathcal{H}_1^n \right\rangle = \sum_{m \neq n} \left\langle \mathcal{H}_0^n \middle| \mathcal{S} \middle| \mathcal{H}_0^m \right\rangle \frac{\left\langle \mathcal{H}_0^m \middle| \mathcal{S} \middle| \mathcal{H}_0^n \right\rangle}{\left(\mathcal{H}_0^m - \mathcal{H}_0^n \right)} \\ &= \sum_{m \neq n} \frac{\left| \left\langle \mathcal{H}_0^m \middle| \mathcal{S} \middle| \mathcal{H}_0^n \right\rangle \right|^2}{\left(\mathcal{H}_0^m - \mathcal{H}_0^n \right)} \end{aligned} \qquad [\text{ A-7b }]$$